THE STRUCTURE OF EMISSION LINES

By Frank Hoyt

Ryerson Physical Laboratory, University of Chicago

Abstract

A method for obtaining the **intensity distribution in a spectral line** is derived from Dirac's quantum theory of the radiation field. The calculations are carried out for the case of emission from a first excited state (resonance line) and show that the intensity of frequency ν is, in this case, proportional to $1/[4\pi^2(\nu_0-\nu)^2+(A.2)^2]$ were A is the rate at which atoms are leaving the upper state and ν_0 is the frequency of the transition. The half-width is therefore $1/2\pi$ times the Einstein probability coefficient for spontaneous transition to the lower state. The more general case where the lower state has a finite life time is not treated.

A general method for the treatment of radiation problems, which is essentially Weyl's modification of Dirac's method, is briefly described.

A NY theory of radiation predicts a finite width for emission lines, even under experimental conditions which eliminate Doppler effect and pressure broadening. Classically this "natural width" is attributed to the damping of the atomic oscillations which must accompany an emission of energy, and in the quantum theory a similar result is to be expected from the correspondence principle, the rate of damping being the total rate at which atoms are leaving the upper state. The calculations of the present paper confirm this expectation for the case of a resonance line,[1] and a formula is derived for the structure of the line. The method of treating the radiation field, which is that of Dirac as modified by Weyl,[2] is briefly described, and appears as a very natural extension of the usual procedure of wave mechanics.

The Radiation Field

If the configuration of a dynamical system can be described by any number of variables and the equations of motion written in the Hamiltonian form, the methods of wave mechanics are applicable. If the system is a radiation field the number of variables is infinite; nevertheless, if questions of mathematical rigor are disregarded, it seems possible to set up a wave equation and interpret its solutions in the usual way when these variables form a denumerable set, such as the development coefficients of the field vectors in a system of orthogonal functions.

Consider an electromagnetic field inside a cubical inclosure whose dimensions will eventually be allowed to become infinite. It can be completely specified by the values of a vector potential A at all points inside the in-

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[1] Regarding the generalization to other cases see the note at the end of this paper.

[2] P. A. M. Dirac, Proc. Roy. Soc. **A114**, 243, 710 (1927); H. Weyl, Gruppentheorie und Quantenmechanik, Leipzig (1928) p. 89.

closure, provided A satisfies the relation $\nabla \cdot A = 0$. The fields are then $E = -(1/c)\,(\partial A/\partial t)$, $H = \nabla \times A$ and the total energy is

$$\mathcal{E} = \frac{1}{8\pi} \int \left[\frac{1}{c^2}\left(\frac{\partial A}{\partial t}\right)^2 + (\nabla \times A)^2\right] dv. \tag{1}$$

The "equations of motion" are then the Maxwell field equations, but they may be replaced by the single equation

$$\nabla^2 A - \frac{1}{c^2}\,\frac{\partial^2 A}{\partial t^2} = 0,$$

which is completely equivalent to them. It is readily shown that this equation gives a set of ordinary equations for the development coefficients of A.[2] If a Fourier development is chosen the variables have a direct physical significance; we therefore write, for the field within a cube of length L,

$$A = \sum_\tau a_\tau \exp 2\pi i\, k_\tau \cdot r, \qquad a_{-\tau} = a_\tau{}^* \tag{3}$$

where $a_\tau = a_{\tau 1} + a_{\tau 2}$ is a complex vector, r a real vector from the center of the box, and k_τ is the vector with components τ_1/L, τ_2/L, τ_3/L. The integers τ_1, τ_2, τ_3 take on all positive and negative values. The condition $\nabla \cdot A = 0$ is fulfilled by taking a_τ perpendicular to k_τ, and a_τ is then specified by only two components.

Substituting Eq. (3) in Eq. (2), regarding the a_τ as functions of the time, gives the equations

$$\frac{d^2 a_\tau}{dt^2} + 4\pi^2 c^2 k_\tau{}^2 a_\tau = 0$$

which are the equations of motion for a system of independent linear oscillators with frequencies $\nu_\tau{}^2 = c^2 k_\tau{}^2$. On substitution of the solutions in Eq. (3) the field is represented as a linear superposition of plane-polarized, progressive waves, so that classically the a_τ are the amplitudes of such waves.

The Eqs. (3) may be put in canonical form with the Hamiltonian

$$H = \sum_\tau \tfrac{1}{2}\,|\,b_\tau\,|^{\,2} + 2\pi^2\nu_\tau{}^2\,|\,a_\tau\,|^{\,2}$$

where $b_\tau = \dot{a}_\tau$ is the "momentum" conjugate to a_τ. It is easy to show, by substituting Eq. (3) in Eq. (1), that, independently of any boundary conditions,

$$\mathcal{E} = \frac{L^3}{4\pi c^2}\,\sum_\tau \frac{1}{2}\,|\,b_\tau\,|^{\,2} + 2\pi^2\nu_\tau{}^2\,|\,a_\tau\,|^{\,2}$$

Therefore $H = (L^3/4\pi c^2)\,\mathcal{E}$, and the Hamiltonian is the energy of the inclosure, except for a constant factor.

For the purpose of quantization it is preferable to have real, scalar quantities for the variables instead of the complex vectors a_τ, and to have

the Hamiltonian equal to the energy. This is accomplished by using a slightly different representation of A. Let $l_r^{(\sigma)}(\sigma=1,\ 2)$ be two unit vectors chosen in some definite way in the plane perpendicular to k_r (plane of polarization), and $a_\rho^{(\sigma)}$ ($\rho=1, 2$) be the components of a_{r1} and a_{r2} in these directions. Then, on making use of the reality condition $a_{-r}=a_r^*$ Eq. (3) may be written

$$A = 2\sum_r(\tau_1 \geqq 0)a_{r1}^{(1)}l_r^{(1)}\cos 2\pi k_r \cdot r - a_{r2}^{(1)}l^{(1)}\sin 2\pi k_r \cdot r$$
$$+ a_{r1}^{(2)}l_r^{(2)}\cos 2\pi k_r \cdot r - a_{r2}^{(2)}l_r^{(2)}\sin 2\pi k_r \cdot r$$

if one of the integers, τ_1, is restricted to positive values. It is therefore seen that any real vector A satisfying the condition $\nabla \cdot A = 0$ can be written in the form

$$A = \sum_r(\tau_1 \geqq 0) \sum_{\rho=1}^{2} \sum_{\sigma=1}^{2} q_{r\rho\sigma}\ A_{r\rho},$$

where $q_{r\rho\sigma}$ replaces $\pm 2a_{r\rho}^{(\sigma)}$ and the $A_{r\rho\sigma}$ are orthogonal vector functions into which, for convenience, a constant factor $2c(2\pi/L^3)^{1/2}$ has been introduced; explicitly they are

$$A_{r1\sigma} = 2c(2\pi/L^3)^{1/2}l_r^{(\sigma)}\cos 2\pi k_r \cdot r,$$

$$A_{r2\sigma} = 2c(2\pi/L^3)^{1/2}l_r^{(\sigma)}\sin 2\pi k_r \cdot r. \tag{5}$$

The constant factor has been so chosen that the energy is simply the Hamiltonian

$$\mathcal{E} = H_R = \sum_{r,\rho,\sigma}(\tau_1 \geqq 0)[\tfrac{1}{2}p^2_{r\rho\sigma} + 2\pi^2\nu_r^2q_{r\rho\sigma}^2],$$

where $p_{r\rho\sigma} = \dot{q}_{r\rho\sigma}$. The index τ determines the frequency and direction of a plane wave component, ρ distinguishes cosine from sine terms, and σ gives the direction of polarization.

For simplicity the vector potential may accordingly be written

$$A = \sum_\alpha q_\alpha A_\alpha \tag{6}$$

where α stands for τ, ρ, σ. The Hamiltonian for the radiation field is then

$$H_R = \sum_\alpha \tfrac{1}{2}p_\alpha^2 + 2\pi^2\nu_\alpha^2 q_\alpha^2 \tag{7}$$

where q_α and p_α are real.

Wave Mechanics of an Atom in a Radiation Field

Suppose an atom, represented for simplicity as a single electron (mass μ, charge $-e$, momentum p) is placed at the center of the box. The classical Hamiltonian for the system "atom plus radiation field," neglecting spin and assuming $v^2/c^2 < <1$, can then be written

$$H = \frac{1}{2\mu}\left(p + \frac{e}{c}A\right)^2 + U + H_R$$

where U is the potential energy of the electron in the field of the nucleus and A and H_R are the functions of q_α, p_α given by Eqs. (6) and (7). The corresponding wave equation is $H\psi + (h/2\pi i)\partial\psi/\partial t$ where H is the operator obtained by making the substitutions $p = (h/2\pi i)\nabla$, $p_\alpha = (h/2\pi i)\partial/\partial q_\alpha$ and ψ is a function of the time t, the atomic coordinates r, and the variables q_α which specify the field. This wave equation may be written

$$(H_0 + V)\psi(t, r, q_\alpha) + \frac{h}{2\pi i}\frac{\partial\psi}{\partial t} = 0$$

with $V = H_1 + H_2$, where

$$H_0 = -\frac{h^2}{8\pi^2\mu}\nabla^2 + U + \sum_\alpha\left(-\frac{h^2}{8\pi^2}\frac{\partial^2}{\partial q_\alpha^2} + 2\pi^2\nu_\alpha^2 q_\alpha^2\right) \tag{8}$$

$$H_1 = \frac{eh}{2\pi i\mu c}\sum_\alpha q_\alpha A_\alpha\cdot\nabla \tag{9}$$

$$H_2 = \frac{e^2}{2\mu c^2}\sum_{\alpha,\beta}q_\alpha q_\beta A_\alpha\cdot A_\beta. \tag{10}$$

(The operators A and ∇ are commutative when $\nabla\cdot A = 0$.)

Such a wave equation differs from those usually encountered only in the fact that the number of variables is infinite. It may be treated by regarding V as a perturbation and using the method of variation of constants. This gives the solution in the form

$$\psi = \sum_a c_a(t)u_a(\xi)e^{-(2\pi i/h)E_a t},$$

where $\xi = r$, q_1, q_2, $\cdots$, and the u_a are the normalized characteristic functions of the unperturbed problem. The c_a are determined by the differential equations

$$-\frac{h}{2\pi i}\dot{c}_a = \sum_b V(ab)e^{-(2\pi i/h)E_a t}c_b \tag{11}$$

where $V(ab)$ is the perturbation matrix

$$V(ab) = \int u_a^* V u_b d\xi.$$

In the case of the present wave equation the characteristic functions of the unperturbed system are

$$u_a = u_k(r)\prod_\alpha u_{r_\alpha}(q_\alpha)$$

where $u_k(r)$ is the k-th characteristic function for the atom alone, and u_{r_α} is a Hermite orthogonal function, since the operator in H_0 that involves q_α is simply that for the energy of a linear oscillator (of unit mass). The corresponding characteristic value of the energy is

$$E_a = E_k + \sum_\alpha (r_\alpha + \tfrac{1}{2}) h\nu_\alpha.$$

A state of the unperturbed system is thus represented by a complex of quantum numbers $a \equiv (k; r_1, r_2, \cdots,)$ and the c_a may be given the customary probability interpretation (which is also a consequence of the general transformation theory). That is, $|c(t, k; r_1, r_2, \cdots, |^2$ measures the probability of finding the atom to have the energy E_k and the α-th radiation component to have the energy $(r_\alpha + \tfrac{1}{2}) h\nu_\alpha$, if the interaction between the atom and field is suddenly destroyed or becomes vanishingly small at time t. The energy of a field component in its lowest state $r_\alpha = 0$ is still $(1/2)h\nu_\alpha$; this "zero-point energy" must be regarded as undetectable in the form of radiation.

PROPERTIES OF THE PERTURBATION MATRIX

The quantities $|V(ab)|^2$ eventually measure transition probabilities from state b to state a, and certain of their formal properties are of importance. Using Dirac's notation for a matrix element we may write $V(ab)$ $= (k; r_1, \cdots, |H_1| l; s_1, \cdots,) + (k; r_1, \cdots, |H_2| l; s_1, \cdots,)$. A given element of $H_1 = (eh/2\pi i\mu c)A \cdot \nabla$ is of the form

$$(k; r_1, \cdots | H_1 | l; s_1 \cdots) = \frac{eh}{2\pi i\mu c} \sum_\alpha \int u_k^* A_\alpha \cdot \nabla u_l dv$$

$$\cdot \int \cdots \int q_\alpha u_{r_1}^* \cdots u_{s_1} \cdots dq_1 \cdots.$$

Since $\int q_\alpha u_{r_\alpha}^* u_{s_\alpha} dq_\alpha$ is the (r_α, s_α) element of the coordinate matrix of a linear oscillator it is different from zero only when $s_\alpha = r_\alpha \pm 1$. Thus the only elements of H_1 different from zero are those corresponding to transitions in which the quantum number of only one radiation component changes by ± 1, those of the others remaining constant. Inserting the well-known expressions for the coordinate matrices of the linear oscillator and the values of A_α given in Eq. (5) the non-vanishing elements of H_1 may be written

$$(k; r_1, \cdots r_\alpha \cdots | H_1 | l; r_1, \cdots r_\alpha - 1, \cdots) = \left(\frac{hr_\alpha}{\pi\nu_\alpha}\right)^{1/2} \frac{e}{\mu} I_\alpha \cdot P_\alpha(kl) \cdot \frac{1}{L^3} \qquad (12)$$

$$(k; r_1, \cdots r_\alpha \cdots | H_1 | l; r_1, \cdots r_\alpha + 1, \cdots) = \left(\frac{h(r_\alpha + 1)}{\pi\nu_\alpha}\right)^{1/2} \frac{e}{\mu} I_\alpha \cdot P_\alpha(kl) \cdot \frac{1}{L^3} \qquad (13)$$

where

$$P_{\tau\rho\sigma}(kl) = \frac{h}{2\pi i} \int \begin{Bmatrix} \cos \\ \sin \end{Bmatrix} 2\pi k_\tau \cdot r u_k^* \nabla u_l dv \qquad \begin{pmatrix} \cos & \text{for} & \rho = 1 \\ \sin & \text{for} & \rho = 2 \end{pmatrix} (14)$$

Elements of the first kind correspond to transitions of the atom from state l to state k accompanied by emission of radiant energy, those of the second kind to the same atomic transition accompanied by absorption.

It will be seen at once that for radiation components of not too short wave-length $P_\alpha(kl)$ reduces to the (kl) element of the atomic momentum. This will be the case when the trigonometric factor may be replaced without appreciable error by its value at the nucleus. In general this means $\nu_\alpha = c \, |k_\alpha| < < 10^{-8}$ cm, so that for visible light

$$P_{\tau1\sigma}(kl) = p(kl) = 2\pi i \mu \nu(kl) r(kl)$$
$$P_{\tau2\sigma}(kl) = 0.$$
(14a)

As will appear later the most important matrix elements for spontaneous emission are those of the form $(k; 0, \cdots, r_\alpha = 1, 0, \cdots, |H_1| l; 0, \cdots)$, which may be abbreviated to $(k1_\alpha |H_1| l0)$, if it is understood that all quantum numbers not specified are zero. Their squares

$$| (kl_\alpha | H_1 | l0) |^2 = \frac{h}{\pi \nu_\alpha} \left(\frac{e}{\mu} \right)^2 | I_\alpha \cdot P_\alpha(kl) |^2 \cdot \frac{1}{L^3}$$

refer to transitions of the atom accompanied by "emission of one quantum" of a definite frequency, direction and state of polarization specified by α. In their dependence on frequency and direction as specified by τ they are continuously variable in the limit $L \doteq \infty$, and may be regarded as point functions defined at the points with rectangular coordinates τ_1/L, τ_2/L, τ_3/L, in a three dimensional "k-space." The volume element $dk_1 \, dk_2 \, dk_3$ in this space is $1/L^3$. It is more convenient, however, to use a system of spherical coordinates, as in this case $\nu/c = |\mathbf{k}|$ represents distance from the origin. If $d\Omega$ is an infinitesimal solid angle in the direction of k we may write for the volume element

$$dk_1 dk_2 dk_3 = (\nu^2/c^3) d\nu d\Omega.$$

Direction and frequency are now specified by continuous variables ν and $\Omega = (\theta, \phi)$ which replace the index τ so that

$$| (k, 1_{\nu\rho\sigma} | H_1 | l0) |^2 = \frac{h}{\pi\nu} \left(\frac{e}{\mu} \right)^2 | I_\sigma(\nu, \Omega) \cdot P_\rho(kl; \nu, \Omega) |^2 \cdot \frac{\nu^2}{c^3} d\nu d\Omega. \quad (15)$$

It will be convenient to replace sums of such elements over τ by integrals over ν and Ω.

The matrix elements of $H_2 = (e^2/2\mu c^2) A \cdot A$, on the other hand, are of the form

$$(k; r_1, \cdots | H_1 | l; s_1, \cdots) = \frac{e^2}{2\mu c^2} \sum_{\alpha,\beta} \int A_\alpha \cdot A_\beta u_k^* u_l dv$$

$$\cdot \int \cdots \int q_\alpha q_\beta \cdot u_{,1}^* \cdots u_{s_1} \cdots dq_1 \cdots .$$

For optical frequencies they will vanish except when $k = l$, i.e. when the state of the atom does not change; at the same time *two* radiation components can change their quantum numbers, again by ± 1. These elements are responsible for direct scattering of light (Dirac's true scattering) but are unimportant for spontaneous emission. Since they are of the second order in $(1/L^3)^{1/2}$ they are negligible when added to elements of H_1.

Spontaneous Emission of a Resonance Line

The usual method of solving the variation equations (11) is to substitute in the right hand members the values of the c_a at time $t = 0$. Integration then gives an approximation which is valid for a short time—in general short compared to the life-time of an excited state. On re-substitution, higher approximations may be found. By proceeding in this way it is possible to obtain all of Dirac's results for emission, absorption, and dispersion. In fact, the present equations differ from those of Dirac only in that the c's give the probability of finding a system in a given stationary state, while his give the probability of finding a given distribution of a number of systems among the various stationary states.

This method of solution is inadequate, however, if we wish to investigate the structure of a line within its natural width, as may be seen by appealing to the uncertainty principle. As applied to energy and time this states that any limitation Δt in the time of an energy measurement will introduce an unavoidable uncertainty in the energy of amount $\Delta E = h/\Delta t$. For a component of the radiation field $E \approx h\nu$, and hence

$$\Delta \nu \approx \frac{1}{\Delta t}.$$

It is well known that the natural width of an emission line is approximately $1/T$, where T is the life-time of the upper state. Hence a solution of Eqs. (11) which is valid only for $t < < T$ cannot predict the result of a frequency measurement of accuracy greater than $\Delta \nu = 1/T$. Actually, as Pauli has shown,[3] Dirac's results give only the total probability of finding a light quantum in a given range of stationary states extending over the natural width.

It is possible to obtain, however, a solution of the variation equations which is valid for any value of t *much greater* than the life-time. This will not be subject to the foregoing restrictions, and we shall see that it gives a reasonable formula for the shape of an emission line.

Written explicitly the Eqs. (11) are

$$- \frac{h}{2\pi i} \dot{c}(k; r_1, \cdots) = \sum_{l,\alpha} (k; r_1, \cdots \mid H_1 \mid l; r_1, \cdots r_\alpha \pm 1, \cdots)$$

$$e^{(2\pi i/h)(E_k - E_l + h\nu_\alpha)t} c(l; r_1, \cdots r_\alpha \pm 1, \cdots)$$

$$+ \text{ terms in } H_2$$

[3] Probleme der Modernen Physik, Leipzig, 1928, p. 30.

where the $\pm$ sign means inclusion of both terms in the sums. If we are interested only in the solutions for large values of the time it will be legitimate to retain on the right only those terms which are constant or vary slowly with the time, since the effect of those which vary rapidly and periodically will average out. The "resonance" or "secular" terms are those for which $E_k = E_l \pm h\nu_\alpha$ is zero or very small, so that they are just those which correspond to transitions in which the total energy is conserved.

To describe spontaneous emission we wish a solution for initial conditions such that at time $t = 0$ it is certain that all atoms are in an excited state m, while all radiation components are unexcited. We therefore suppose only $c(m; 0, \cdots)$, is initially different from zero. From the infinite set of equations it is then possible to discard any sub-set containing only c's which are not coupled with $c(m; 0, \cdots)$ since such a set will have only the trivial solution that all the c's which it contains remain practically zero. Terms in H_2 may also be neglected compared to those in H_1 as they are of the second order in $(1/L^3)^{1/2}$. At the same time we may retain only the resonance terms. If this process of elimination is carried out consistently for the special case that m is the first excited state of the atom, so the only state of lower energy is the normal state $k = n$ the only equations which survive are the following:

$$- \frac{h}{2\pi i}\dot{c}(n1_\alpha) = H_1(\alpha 0)e^{-2\pi i(\nu_0 - \nu_\alpha)t}c(m0), \tag{16}$$

$$- \frac{h}{2\pi i}\dot{c}(m0) = H_1(0\alpha)e^{2\pi i(\nu_0 - \nu_\alpha)t}c(n1_\alpha). \tag{17}$$

where $(E_m - E_n)/h = \nu_0$ and $H_1(\alpha 0)$ is put for $(n1_\alpha |H_1| m0)$.

A solution of these equations which is valid when only $c(m0)$ is initially different from zero may be obtained in the following manner: From Eqs. (16),

$$\dot{c}(n1_\alpha) = - \frac{2\pi i}{h}H_1(\alpha 0) \int_0^t e^{-2\pi i(\nu_0 - \nu_\alpha)t}c(m0)ds$$

and substituting these integrals in Eq. (17) gives the integral equation

$$\dot{c}(m0) = - \left(\frac{2\pi}{h}\right)^2 \sum_\alpha | H_1(\alpha 0) |^2 e^{2\pi i(\nu_0 - \nu_\alpha)t}$$

$$\int_0^t e^{-2\pi i(\nu_0 - \nu_\alpha)s}c(m0)ds \tag{18}$$

for $c(m0)$ as a function of the time.

The sum with respect to α may be partly replaced by an integral, since, as already explained, $|H_1(\alpha 0)|^2$ is a continuously varying function of ν and Ω in the limit $L \doteq \infty$. From Eq. (15) it is seen to be of the form

$$| H_1(\alpha 0) |^2 = f_{\rho\sigma}(\nu, \Omega)\nu d\nu d\Omega, \tag{19}$$

where

$$f_{\rho\sigma}(\nu,\ \Omega)\ =\ \frac{h}{\pi c^3}\Big(\frac{e}{\mu}\Big)^2 \big|\ I(\Omega)\cdot \boldsymbol{P}_\rho(nm;\ \nu,\ \Omega)\ \big|^2.\tag{20}$$

Eq. (18) then becomes

$$\dot{c}(m0)\ =\ -\Big(\frac{2\pi}{h}\Big)^2\ \sum_{\rho,\sigma}\ \int_0^{2\pi}\! d\Omega\ \int \nu\Big\{f_{\rho\sigma}e^{2\pi i(\nu_0-\nu)t}$$
$$\int_0^t e^{-2\pi i(\nu_0-\nu)s}c(m0)ds\Big\}d\nu.$$

(The integration with respect to Ω is only over a hemisphere because of the restriction $\tau_1 \geqq 0$.)

It will now be shown that Eq. (18) has a solution of the form $c(m0)$ $= Ce^{-\kappa t}$, and κ will be determined. Substituting this expression in Eq. (18) gives

$$\kappa e^{-\kappa t}\ =\ -\Big(\frac{2\pi}{h}\Big)^2\frac{1}{2\pi i}\ \sum_{\rho,\sigma}\ \int d\Omega\ \int f_{\rho\sigma}\frac{e^{2\pi i(\nu_0-\nu)t}-e^{-\kappa t}}{\nu-\nu_0+i\dfrac{\kappa}{2\pi}}\nu d\nu.\tag{21}$$

The integral with respect to ν may be written

$$I\ =\ \int F(\nu)\frac{e^{2\pi i(\nu_0-\nu)t}}{\nu-\nu_0+i\dfrac{\kappa}{2\pi}}d\nu$$

$$-\ e^{-\kappa t}\int F(\nu)\frac{\nu-\nu_0}{(\nu-\nu_0)^2+\Big(\dfrac{\kappa}{2\pi}\Big)^2}d\nu$$

$$+\ i\frac{\kappa}{2\pi}e^{-\kappa t}\int F(\nu)\frac{1}{(\nu-\nu_0)^2+\Big(\dfrac{\kappa}{2\pi}\Big)^2}d\nu,$$

where $F(\nu) = \nu f_{\rho\sigma}$. The three integrals may be evaluated without difficulty when it is assumed that κ is vanishingly small compared to ν_0 and that $F(\nu)$ vasnishes for large values of ν in such a way that the integrals converge for high frequencies. The first assumption is certainly valid, since, as will be seen, 2κ is the transition probability; the second has not been rigorously proved, but has been assumed by Dirac in his calculations, and is plausible because $F(\nu)$ contains factors of the form $\int \cos 2\pi k \cdot ru_n{}^*\Delta u_m dv$ which vanish for high frequencies. The limits of integration may then be extended from 0 to ∞, and $F(\nu)$ replaced by $F(\nu_0)$, since, because of the resonance when $\nu = \nu_0$ the contribution to the integral near the resonance point is the predominant part. The first integral may be extended to a closed path in the

complex plane and by Cauchy's theorem its value is $= 2\pi i\ F(\nu_0)e^{-\kappa t}$. The second vanishes because of the factor $\nu_0 - \nu$, while the last may be reduced to the form $\int_{+\infty}^{-\infty} d\xi/(\xi^2 + a^2) = \pi/a$ and contributes $i\pi F(\nu_0)e^{-\kappa t}$. Hence

$$I = -\ \pi i\nu_0 f_{\rho\sigma}(\nu_0,\ \Omega)e^{-\kappa t},$$

and Eq. (18) is satisfied with

$$\kappa = \frac{1}{2}\left(\frac{2\pi}{h}\right)^2 \nu_0 \sum_{\mu\sigma}\ \int d\Omega f_{\rho\sigma}(\nu_0,\ \Omega). \tag{22}$$

The solution of the set of differential equations is completed by substituting $c(mo) = c^0(mo)e^{-\kappa t}$ in Eqs. (16) and integrating, which gives

$$c(n1_\alpha) = c^{(0)}(m0)\frac{2\pi i}{h}H_1(\alpha 0)\frac{e^{-\kappa t}e^{-2\pi i(\nu_0 - \alpha)t} - 1}{2\pi i(\nu_0 - \nu_\alpha) + \kappa} \tag{23}$$

$$c(m0) = c^{(0)}(m0)e^{-\kappa t}. \tag{24}$$

Turning to the physical interpretation of the results just obtained, it is seen from Eq. (24) that the number of atoms in the upper state m falls off exponentially with the time, since $|c(m0)|^2$ is the total probability of finding the atom in state m. This number is proportional to $e^{-2\kappa/t}$, so that $\kappa = (1/2)A$, where A is the Einstein probability coefficient for spontaneous transition. (It will be shown presently that the value of A given by Eq. (22) coincides with that derived from the correspondence principle.) From Eq. (23), on squaring, we obtain the total probability of finding the αth radiation component to have the energy $h\nu_\alpha$. For $t > > 1/\kappa$ this is

$$|\ c(n1_\alpha)\ |^{\ 2} = |\ c^{(0)}(m0)\ |^{\ 2}\frac{\left|\dfrac{2\pi}{h}\ H_1(\alpha 0)\right|^2}{4\pi^2(\nu_0 - \nu_\alpha)^2 + \left(\dfrac{A}{2}\right)^2}$$

which gives the final energy distribution in the line. (For sufficiently large values of the time the atom and field can certainly be regarded as uncoupled.) On summing over all values of α it can be shown that the total energy is $|c^0(m0)|^2 h\nu_0$, as it must be. Since, for $\nu_\alpha \approx \nu_0$, $|H_1(\alpha 0)|^2$ can be regarded as independent of α, and since, in the limit $L \doteq \infty$, $|H_1(\alpha 0)|^2$ is proportional to $d\nu$, the intensity $I(\nu)$ per unit frequency interval is

$$I(\nu) = \text{const}\frac{1}{4\pi^2(\nu_0 - \nu)^2 + \left(\dfrac{A}{2}\right)^2}. \tag{25}$$

This is just the intensity distribution calculated from the Fourier analysis of a classical oscillator with damping constant $(1/2)A$. Since this damping of the amplitude of the virtual oscillator is just what is required to preserve the energy balance when the atoms leave the upper state, according to

Einstein's law, at rate A, it is seen that Eq. (25) gives the result to be expected from the correspondence principle.[5] The half-width (width at half maximum is readily seen to be $(1/2\pi)A$, or $(1/2\pi)$ times the reciprocal of the lifetime of the upper state.

In conclusion it will be shown that the value of κ given by Eq. (22) is actually $\frac{1}{2}$ the usual expression for the probability coefficient:

$$A(mn) = \frac{(2\pi\nu_0)^4}{h\nu_0}\left(\frac{2\iota^2}{3c^3}\right)2 \mid r(mn) \mid^2$$

derived from the correspondence principle on the assumption that only dipole radiation need be considered. Under these conditions (not too short wave-length) the factor $\Sigma_\rho \mid I_\sigma \cdot P_\rho(\nu_0, \Omega) \mid^2$ occuring in Eq. (22) becomes simply $4\pi^2\mu\nu_0^2 \mid I_\sigma \cdot r(mn) \mid^2$ (Cf. Eq. (14a)). If the space degeneracy of the atom is not removed by an external field the $\cos^2$ in the scalar product may be averaged over all orientations of the atom, introducing a factor of $1/3$ and removing any dependence on the direction of polarization (σ) and Ω. With this simplification it is readily seen that κ is $1/2$ the value of $A(mn)$ given by Eq. (26). For short wave-lengths the factor $\cos 2\pi k \cdot r$ in P cannot be regarded as unity. It can be shown, however, that in this case κ is still one half the rate of emission of radiant energy calculated classically from the Schrödinger charge and current density associated with the transition, the trigonometric factor taking care of the retardation.

The method which has been used for emission lines is obviously capable of extension to the case of absorption under various conditions, and the results will be discussed in a future paper.

Note added in proof: Since the above article was sent to press a paper has been published by Weisskopf and Wigner* on the natural widths of emission lines.

Comparison with their results showed an error in the author's generalization of the above results to the case of lines other than a resonance line. A paragraph dealing with this generalization has therefore been deleted in the proof. Weisskopf and Wigner arrive at the important conclusion that the half-width in the general case is $1/2$ times the sum of the total probabilities of spontaneous transition from the upper and lower states. Their method is similar to that of the present paper and gives, of course, the same result for a resonance line. Equations equivalent to those on which they base their treatment of other cases can be derived from Eqs. (11) above.

[5] Cf. W. Pauli, Handbuch der Physik, Vol. XXIII, p. 70.
* Zeits. f. Physik **63**, 54 (1930).